

TECHNICAL REPORT

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RESEARCH COMPENDIUM OF  
HYDROLYZABLE POLYMERS

by

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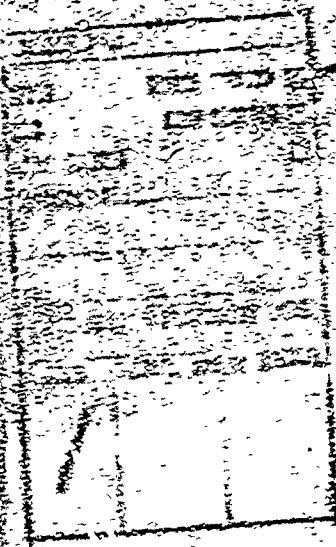
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TECHNICAL REPORT

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RESEARCH COMPOUNDING OF  
NITROSO RUBBER TERPOLYMERS

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## FOREWORD

With the development of nitroso rubber, a copolymer of trifluoro-nitrosomethane and tetrafluoroethylene, it was found that serious problems in processing would be encountered in using this new rubber to fabricate military items. Also it was believed that its low-temperature properties could be improved.

The chief processing problem is centered around crosslinking or vulcanizing the nitroso rubber. Presently, the only successful crosslinking agent for the rubber is the tertiary amine, triethylenetetramine, but this agent is extremely difficult to use. The material is hard to handle on a large scale because of its very fast chemical reaction; also the resulting vulcanizates have low tensile strength and are unstable at high temperatures. Although better in its low-temperature properties than most of the commercial oil-resistant rubbers, nitroso rubber can be used only above -40°F.

To develop nitroso rubbers having improved processing and low-temperature characteristics, a series of nitroso rubber terpolymers was made by the Peninsular ChemResearch, Incorporated, under Army Contract DA19-129-AMC-152, and by the Thiokol Chemical Corporation, under Army Contract DA19-129-AMC-69. For improved processing, they added a third monomer containing chemical functional groups to aid the crosslinking or vulcanization. For improved low-temperature properties, a third monomer was sought that would improve the chain flexibility and internal plasticization. This report describes the compounding studies of these experimental terpolymers.

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## ABSTRACT

Terpolymers were synthesized to give nitroso rubbers having improved processing characteristics and improved low-temperature properties. The terpolymers fall into six types: aromatic-containing, bromine- or chlorine-containing, hydrogen-containing, diene-containing, ester-containing, and miscellaneous. Processing studies were conducted based on the reactive chemical sites contained in the terpolymer. Low-temperature property studies were confined to differential thermal analysis determinations of the second-order transition,  $T_g$ , temperatures. The best processing results were obtained with dichlorobenzoyl peroxide crosslinked esters. The low-temperature properties of the terpolymers show promise for an improved processible nitroso rubber.

## RESEARCH COMPOUNDING OF NITROSO RUBBER TERPOLYMERS

### I. Introduction

Nitroso rubber is a copolymer of trifluoronitrosomethane and tetrafluoroethylene. This new rubber, although having unusual flame-resistant properties, excellent chemical resistance, and good low-temperature properties, is not being used to fabricate military end-items. Previous work<sup>(1)</sup> has shown that this rubber is very difficult to process and compound. The only successful vulcanizing agent used to date has been the tertiary amine, triethylenetetramine. This agent is very reactive; the reactivity (curing reaction) starts on the rubber mill before the compounded stock can be moved to the press for complete curing. Also, the copolymer has a tendency to sponge in the presence of the amine; thus the vulcanizates are porous and have very poor tensile strength.

A program was initiated to produce new nitroso rubbers in which a third monomer was introduced during polymerization. The third monomer was selected on the basis of its having a) a chemical functional group that would offer a site for crosslinking and b) internal plasticization, or "joints" or sites of selective chain rotation, that might improve the low-temperature properties of the base copolymer. A series of nitroso rubber terpolymers (copolymer plus a third monomer) was prepared and evaluated, namely, aromatic-containing; bromine- or chlorine-containing, hydrogen-containing, diene-containing, ester-containing, and miscellaneous.

The purpose of research compounding is to develop the valuable properties of finished rubber products from the properties of basic rubbers. Raw, uncompounded rubber has very few if any useful properties.

The techniques required for the development of useful products vary with the basic properties of the raw rubber. Further, research compounding must always concern itself with the fundamental fact of large-scale factory processing, for any compounding technique that cannot be scaled up to factory production will have very limited military application.

The present method of compounding nitroso rubber gives vulcanizates of doubtful value for end-item application and of doubtful scale-up capability. Only a limited number of valuable properties can be developed in items from this rubber.

The compounding program now underway has considered as the third monomer only those functional groups that will assist in crosslinking and are amenable to factory production. Also considered were some monomers designed to give raw rubbers with improved low-temperature properties.

### II. Materials

The materials covered in this study, together with their glass

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<sup>(1)</sup>Griffis, C.B., Research Compounding of Nitroso Rubber, Technical Report C&OM-13, September 1965.



transition and onset of deterioration temperatures, are listed in Table I (see Appendix for explanation of code). The rubbers were compounded and cured with various recipes, cure times, and temperatures.

### III. Test Methods

The following test methods were used:

	<u>ASTM No.</u>
Tensile Strength	D412-62T
Ultimate Elongation	D412-62T
Hardness	D676-59T

Differential thermal analysis data were obtained with a DuPont Model 900 differential thermal analyzer. All determinations were made under the following conditions:

Sample size, 4 mm	Atmosphere, Ar <sub>2</sub> @ 760 mm
Reference, glass beads	Temperature scale, 50
Rate of heating, 15°C per min.	Baseline slope 0.

The symbols  $T_g$ ,  $T_c$ , and  $T_d$  are used in conjunction with these results. The  $T_g$  value represents the second-order transition temperature, the  $T_c$  value represents the onset of crosslinking temperature, and  $T_d$  value represents the onset-of-deterioration temperature.

### IV. Results and Discussion








#### A. Differential Thermal Analysis

The aromatic-type terpolymers were designed to give improved low-temperature properties. At first glance, the glass transition results (Table I) may seem at odds with this objective. For example, by increasing the aromatic pentafluoronitrosobenzene, **F**NO, from 2.5 to 10 mole percent, the  $T_g$  was raised from -43 to -35°C. However, if well crosslinked rubber could have been made from these base polymers, there is a good possibility that the vulcanizates containing 5 or 10 mole percent pentafluoronitrosobenzene would have better low-temperature "rubbery" properties; in other words, this third monomer might have internally plasticized the rubber compound much as styrene does in styrene-butadiene rubber. As no good crosslinking agent was found for these polymers, their low-temperature properties were not further evaluated.

The addition of a second halogen atom, such as chlorine or bromine, in the tetrafluoroethylene monomer raised the  $T_g$  temperature abruptly. For example, by increasing the CF<sub>2</sub>CFBr from 8 to 50 mole percent, the  $T_g$  was raised from -46 to +3°C.

TABLE I

## Results of Differential Thermal Analysis of Nitroso Terpolymers

Contractor's Code	Terpolymer Composition	Mole(%)*	Temperature (°C) for	
			Glass Transition** (T <sub>g</sub> )	Onset of Deterioration** (T <sub>d</sub> )
<u>Aromatic</u>				
PC-WO 2	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /  NO	2.5	-43	166
PC-WO 3	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /  NO	5	-39	158
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /  NO	5	-40	182
PC-WO 4	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /  NO	10	-35	152
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /Br  NO	5	-44	166
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /HOOC  NO	5	-43	208
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /HOOC  NO	10	-43	192
<u>Bromine and Chlorine</u>				
PC-CQC 8.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFBr	8	-46	221
PC-CQC 8.2	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFBr	16	-35	189
PC-CQC 8.3	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFBr	25	-21	195
PC-CQC 4.3	CF <sub>3</sub> NO/CF <sub>2</sub> CFBr	50	+ 3	198
PC-WO 71.1	CF <sub>3</sub> NO/CF <sub>2</sub> CFC1	50	-50	290
PC-CQC 12.2	CF <sub>2</sub> CF <sub>2</sub> /BrCF <sub>2</sub> CF <sub>2</sub> NO	50	-17	285
<u>Hydrogen</u>				
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFH	0.8	-47	284
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFH	2	-46	283
Thiokol	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFH	5	-46	245

\* The approximate charge ratio used in polymerization

\*\* For the base, uncompounded rubbers

TABLE I Cont'd

## Results of Differential Thermal Analysis of Nitroso Terpolymers

Contractor's Code	Terpolymer Composition	Mole(%) <sup>*</sup>	Temperature (°C) for	
			Glass Transition** (T <sub>g</sub> )	Onset of Deterioration** (T <sub>d</sub> )
<u>Dienes</u>				
PC-WO 56.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> =CFCF=CF <sub>2</sub>	8	-48	264
PC-WO 13.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> =CFCF=CF <sub>2</sub>	25	-46	- -
PC-WO 64.1	CF <sub>3</sub> NO/CF <sub>2</sub> =CFCF=CF <sub>2</sub>	50	- 7	159
PC-WO 57.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> =CFCH=CH <sub>2</sub>	8	-48	264
PC-WO 68.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> =CFCH=CH <sub>2</sub>	10	-49	201
PC-WO 46.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> =CFCH=CH <sub>2</sub>	16	-54	186
<u>Esters</u>				
PC-WO 81.2	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> C(CF <sub>2</sub> ) <sub>2</sub> NO	3	-48	283
PC-WO 81.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> C(CF <sub>2</sub> ) <sub>2</sub> NO	6	-46	285
PC-WO 80.2	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> C(CF <sub>2</sub> ) <sub>2</sub> NO	10	-47	275
PC-WO 80.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> C(CF <sub>2</sub> ) <sub>3</sub> NO	3	-48	282
PC-WO 80.3	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CH <sub>3</sub> O <sub>2</sub> C(CF <sub>2</sub> ) <sub>3</sub> NO	5	-48	278
<u>Miscellaneous</u>				
PC-WO 54.2	CF <sub>3</sub> NO/CF <sub>2</sub> =CFCF=CF <sub>2</sub> treated with NOC1		-83	197
PC-WO 45.1	CF <sub>3</sub> NO/CF <sub>2</sub> =CFCF=CF <sub>2</sub> treated with CF <sub>3</sub> OF		0	280
PC-WO 51.1	CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> =CFCH=CH <sub>2</sub> treated with CF <sub>3</sub> OF		-46	268

\* The approximate charge ratio used in polymerization

\*\* For the base, uncompounded rubbers

When hydrogen was substituted for one fluorine atom in  $\text{CF}_2\text{CF}_2$  to give  $\text{CF}_2\text{CFH}$  as the third monomer, there was virtually no change in the  $T_g$  temperature when the mole percent was increased from 0.8 to 5.

The diene-containing terpolymers behaved as would be expected. The completely fluorinated ( $\text{CF}_2=\text{CFCH}=\text{CH}_2$ ) butadiene substantially raised the  $T_g$  temperature, while the partially fluorinated ( $\text{CF}_2\text{CFCH}=\text{CH}_2$ ) butadiene lowered the  $T_g$  temperature when increased from 8 to 16 mole percent.

The ester-containing terpolymers showed no improvement in lowering of the  $T_g$  temperature. There was little difference between the  $T_g$  temperature of 3, 6, and 10 mole percent of  $\text{CH}_3\text{O}_2(\text{CF}_2)_2\text{NO}$ , and no difference noted between the 2 and 3 ( $\text{CF}_2$ ) groups in the ester chain. It was noted that all of these polymers had a  $275^\circ\text{C}$  or higher temperature for the onset of deterioration.

It is interesting to note that  $\text{NOCl}$  plasticized the copolymer of  $\text{CF}_3\text{NO}/\text{CF}_2=\text{CFCH}=\text{CF}_2$  to give a  $T_g$  of  $-83^\circ\text{C}$ , which is the lowest recorded for any of the materials tested. When the same copolymer was treated with  $\text{CF}_3\text{OF}$ , the  $T_g$  moved from  $-7$  to  $0^\circ\text{C}$ , which indicates either addition or crosslinking. The addition of  $\text{CF}_3\text{CF}$  to  $\text{CF}_3\text{NO}/\text{CF}_2\text{CF}_2/\text{CF}_2=\text{CFCH}=\text{CH}_2$  had little effect on the  $T_g$  temperature, which indicates that the  $\text{CF}_3\text{OF}$  did not react with this terpolymer.

#### B. Compounding and Test Results

The vulcanizates made with the aromatic-containing terpolymers were all too poor to test (Table II). Very small quantities of these materials were available, in many cases, only enough for one compounding attempt. The bromine-containing aromatic did not cure when a typical bromo-butyl compounding recipe was used (Compound 65-M-16-25). Because no good vulcanizates were made, there was no evaluation of the "rubbery" properties at low temperatures.

None of the reactions investigated resulted in crosslinking the bromine-containing terpolymers (Table III). Standard bromo-butyl peroxide and neoprene-type recipes, and also phenolics, were all tried without success. It was hoped that the PC-CQC 12.2 polymer, which contains  $\text{BrCF}_2\text{CF}_2\text{NO}$ , would react because the bromine is located two ( $\text{CF}_2$ ) groups away from the backbone. There was enough polymer for only one experiment and for this it was decided to use a simple neoprene-type recipe (shown in Compound 65-M-17-13). There was no cure in the press and the differential thermal analysis did not show any evidence of crosslinking.

Table IV gives the compounding recipes and test results of hydrogen-containing terpolymers. There were indications of crosslinking in every experiment attempted. This very definitely indicates that, where there is an available hydrogen atom on a carbon atom that is next to a fluorinated carbon atom, crosslinking can be accomplished. This is evident in the perfluoropropylene/vinylidene fluoride polymers which contain

TABLE II

## Compounding and Test Results - Aromatic Terpolymers


Compound Number	63-M-12			65-M-16
	2	3	4	25
PC-WO 2	100	- -	- -	- -
PC-WO 3	- -	100	- -	- -
PC-WO 4	- -	- -	100	- -
Thiokol (Br  NO)	- -	- -	- -	100
Cab-O-Sil	20	20	20	- -
BMDA	2	2	2	- -
TETA	1.5	1.5	1.5	- -
ZnO	- -	- -	- -	5
MBTS	- -	- -	- -	1
H <sub>2</sub> O	- -	- -	- -	4
Stearic acid	- -	- -	- -	1
Na22	- -	- -	- -	1
Diethyl thiourea	- -	- -	- -	2
Press cure time, min/temp, °F	60/250	60/250	60/250	60/250
Oven cure time, hr/temp, °F	16/212	16/212	16/212	- -
Tensile strength, psi	Cure too poor to test	Cure too poor to test	Cure too poor to test	No cure
Elongation, %	Cure too poor to test	Cure too poor to test	Cure too poor to test	No cure
Hardness, Shore A	Cure too poor to test	Cure too poor to test	Cure too poor to test	No cure
Onset of cross-link, T <sub>c</sub> °C	--	--	None	--
Onset of deterioration, T <sub>d</sub> °C	--	--	138	--

TABLE III

## Compounding and Test Results - Bromine Terpolymers

Compound Number	64-M-16				65-M-17	
	76	77	78	96	1	13
PC-CQC 8.2	100	- -	- -	- -	100	- -
PC-CQC 8.1	- -	100	- -	100	- -	- -
PC-CQC 8.3	- -	- -	100	- -	- -	- -
PC-CQC 12.2	- -	- -	- -	- -	- -	100
HiSil 233	15	10	10	- -	- -	- -
HiSil 303	- -	- -	- -	15	15	15
ZnO	5	5	5	- -	3	5
TMDS	1	- -	- -	- -	- -	- -
MBTS	2	- -	- -	- -	- -	- -
MgO	2	2	2	- -	- -	4
Stearic acid	1	1	- -	- -	- -	0.5
Durez 12687	- -	3	- -	- -	- -	- -
Na22	- -	1.5	- -	- -	- -	- -
DiCup 40	- -	- -	8	4	10	- -
Divinyl benzene	- -	- -	- -	4	- -	- -
1,5 Hexadiene	- -	- -	- -	- -	5	- -
Press cure time, min/temp, °F	60/280	60/280	60/280	60/250	60/250	60/250
Oven cure time, hr/temp, °F	- -	- -	- -	- -	- -	- -
Tensile strength, psi	No cure	No cure	No cure	No cure	No cure	No cure
Elongation, %	No cure	No cure	No cure	No cure	No cure	No cure
Hardness, Shore A						
Onset of cross-link, T <sub>c</sub> <sup>°C</sup>	- -	- -	- -	- -	- -	None
Onset of deterioration, T <sub>d</sub> <sup>°C</sup>	- -	- -	- -	- -	- -	285

TABLE IV

## Compounding and Test Results - Hydrogen Terpolymers

Compound Number	64-M-16				
	51	62	63	66	67
CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFH - 0.8 mole %	100	100	100	- -	- -
CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFH - 2 mole %	- -	- -	- -	100	- -
CF <sub>3</sub> NO/CF <sub>2</sub> CF <sub>2</sub> /CF <sub>2</sub> CFH - 5 mole %	- -	- -	- -	- -	100
HiSil 303	15	15	15	- -	10
ZnO	5	5	- -	- -	- -
HMDA	4	3	2	1.5	2
DyPhos	10	10	- -	- -	- -
TETA	- -	1	1.5	- -	- -
MgO	- -	- -	- -	15	7.5
Silstone 110	- -	- -	- -	10	- -
Press cure time, min/temp, °F	60/250	60/220	60/220	60/250	60/220
Oven cure time, hr/temp, °F	16/212	16/212	16/212	--	--
Tensile strength, psi	200	200	100	- -	- -
Elongation, %	100	125	100	No cure	No cure
Hardness, Shore A	72	65	59	No cure	No cure
Onset of cross-link, T <sub>c</sub> °C	104	- -	- -	120	127
Onset of deterioration, T <sub>d</sub> °C	- -	- -	- -	238	236

repeating units of the following monomers:  $\text{CF}_3\text{CF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$ . None of the vulcanizates made with hydrogen-containing monomers exhibited good physical properties. Apparently new polymerization techniques will have to be developed before good polymers can be made utilizing these monomers.

Although there were several recipes that produced crosslinking, none of the diene-containing terpolymers gave vulcanizates with good physical properties, as is shown in Table V. These materials reacted with TETA, HMDA, and the peroxides. There was no reaction with dichloro-p-xylene, as shown in compound 64-M-16-92. Because of the chemical reactivity of the terpolymers containing dienes, and because of their good low-temperature properties, compounding studies will be continued with this type of polymer.

The ester-containing terpolymers were the most interesting of all those tested, as is shown in Table VI. These rubbers had good low-temperature properties, excellent high-temperature stability, and the capability of being crosslinked with agents that can be adapted to factory production. The best stock made used the recipe shown in 65-M-17-7. Although its tensile strength was only 500 psi, its elongation was 400%, and its hardness 60. This material processes very well; however, it sticks to both rolls of the rubber mill when cold rolls are used. The stock strips easily from the curing mold, which is not characteristic of most of the nitroso rubbers. There appears to be little difference between the curing of the two esters,  $\text{CH}_3\text{O}_2\text{C}(\text{CF}_2)_2\text{NO}$  and the  $\text{CH}_3\text{O}_2\text{C}(\text{CF}_2)_3\text{NO}$ . The extra  $\text{CF}_2$  in the side chain apparently has little effect on the chemical reactivity of the ester group. Although DiCup 40 (dicumylperoxide) will crosslink the polymer, Cadox TS-50 (50% dichlorobenzoyl peroxide) is much more effective. Based on all of the plus factors of this terpolymer, and including non-flammability of the vulcanizate, it is felt that further study of this system is warranted.

## VI. Conclusions

Nitroso rubber terpolymers can be made containing chemical functional groups that can be reacted with many crosslinking agents.

The diene-containing terpolymers show reactivity with dicumyl peroxide.

The bromine-containing terpolymers showed no reactivity in any of the six experiments attempted.

## VII. Recommendations

It is recommended that further work be accomplished with the diene-containing nitroso rubbers. This work should include the preparation of other 1,1,2 trifluorobutadiene-containing terpolymers and continuing research compounding studies.

It is recommended that ester-containing terpolymers be made, with emphasis on those having uniform molecular weight, and that continuing compounding studies be planned with this type of polymer.



TABLE V

## Compounding and Test Results - Diene and Miscellaneous

Compound Number	64-M-16							
	54	59	73	74	75	80	90	92
PC-WO 46.1	100	- -	- -	- -	- -	- -	- -	- -
PC-WO 43.1	- -	100	- -	- -	- -	- -	- -	- -
PC-WO 54.2	- -	- -	100	- -	- -	- -	- -	- -
PC-WO 57.1	- -	- -	- -	100	- -	- -	- -	- -
PC-WO 56.1	- -	- -	- -	- -	100	- -	- -	- -
PC-WO 68.1	- -	- -	- -	- -	- -	- -	100	100
PC-WO 64.1	- -	- -	- -	- -	- -	100	- -	- -
HiSil 303	15	15	10	10	10	10	15	- -
ZnO	- -	- -	5	- -	8	- -	5	- -
DiCup 40	9	- -	8	- -	8	- -	- -	- -
Trimethacrylate	3	- -	- -	- -	- -	- -	- -	- -
TETA	- -	1.5	- -	- -	- -	2	- -	- -
HMDA	- -	2	- -	4	- -	4	- -	- -
MgO	- -	- -	- -	5	- -	- -	- -	- -
Benzoyl peroxide, 50%	- -	- -	- -	- -	- -	- -	4	- -
DyPhos	- -	- -	- -	- -	- -	- -	10	- -
Dichloro-p-xylene	- -	- -	- -	- -	- -	- -	- -	10
Press cure time, min/ temp, °F	60/ 300	60/ 220	60/ 230	60/ 230	60/ 280	60/ 250	60/ 300	60/ 300
Oven cure time, hr/ temp, °F	- -	60/ 212	- -	- -	- -	- -	- -	- -
Tensile strength, psi	Too poor to test	Too poor to test	No cure	100	No cure	No cure	Cure sponged	No cure
Elongation, %				100				
Hardness, Shore A				40				
Onset of cross-link, T <sub>c</sub> °C	109		None	70				
Onset of deterioration, T <sub>d</sub> °C	155		156	- -				

TABLE VI

## Compounding and Test Results - Ester Terpolymers

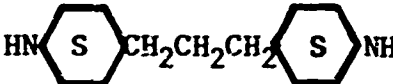
Compound Number	65-M-17							
	6	10	11	2	3	4	5	7
PC-WO 81.2	100	100	100	- -	- -	- -	- -	- -
PC-WO 81.1	- -	- -	- -	100	100	100	100	100
HiSii 303	15	15	- -	10	10	15	15	15
HN  NH	5	- -	- -	- -	- -	- -	- -	- -
ZnO	- -	3	3	3	- -	- -	- -	3
Cadox TS-50	- -	4	4	- -	- -	- -	- -	3
Philblack "O"	- -	- -	30	- -	- -	- -	- -	- -
DiCup 40	- -	- -	- -	5	- -	- -	8	- -
CF <sub>3</sub> NO/CF <sub>2</sub> =CFCF=CF <sub>2</sub>	- -	- -	- -	20	- -	- -	- -	- -
Dibutyltindihydride	- -	- -	- -	- -	10	5	- -	- -
Calcium hydroxide	- -	- -	- -	- -	- -	- -	3	- -
1,5 Hexadiene	- -	- -	- -	- -	- -	- -	- -	2
Press cure time, min/temp, °F	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250
Oven cure time, hr/temp, °F	- -	- -	- -	16/ 212	16/ 212	- -	- -	16/ 212
Tensile strength, psi		400		100				500
Elongation, %	No cure	800	No cure	700	Too poor to test	Too poor to test	No cure	400
Hardness, Shore A	No	62	No	52	Too poor to test	Too poor to test	No	60
Onset of cross-link, T <sub>c</sub> , °C		102		173	98			105
Onset of deterioration, T <sub>d</sub> , °C		262		- -	- -			245

TABLE VI Cont'd

## Compounding and Test Results - Ester Terpolymers

Compound Number	64-M-16						65-M-17		
	100	101	102	103	98	99	8	9	12
PC-WO 80.2	100	100	100	100	- -	- -	- -	- -	- -
PC-WO 80.1	- -	- -	- -	- -	100	100	- -	- -	- -
PC-WO 80.3	- -	- -	- -	- -	- -	- -	100	100	100
HiSil 303	15	15	15	15	15	15	15	15	15
Calcium hydroxide	5	- -	- -	- -	- -	10	- -	- -	- -
DiCup 40	- -	8	- -	- -	- -	- -	- -	- -	- -
Dichloro-p-xylene	- -	- -	10	- -	- -	- -	- -	- -	- -
DyPhos	- -	- -	5	- -	- -	- -	- -	- -	- -
Diethylene glycol	- -	- -	- -	4	- -	- -	- -	- -	- -
Durez 12687	- -	- -	- -	5	- -	- -	- -	- -	- -
Chromium trifluoro acetate	- -	- -	- -	- -	5	5	- -	- -	- -
ZnO	- -	- -	- -	- -	- -	- -	3	3	3
Cadox TS-50	- -	- -	- -	- -	- -	- -	3	3	4
1,5 Hexadiene	- -	- -	- -	- -	- -	- -	- -	2	- -
Press cure time, min/temp, °F	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250	60/ 250
Oven cure time, hr/temp, °F	- -	- -	- -	- -	- -	- -	48/ 212	48/ 212	48/ 212
Tensile strength, psi							150	100	100
Elongation, %	e r	e r	e r	e r	e r	e r	400	200	500
Hardness, Shore A	C C	C C	C C	C C	C C	C C	58	52	58
Onset of cross-link, T <sub>c</sub> °C	o N	o N	o N	o N	o N	o N	108		
Onset of deterioration, T <sub>d</sub> °C							165		

# APPENDIX

## Compounding Materials

<u>Material</u>	<u>Trade Name</u>	<u>Supplier</u>
Silicon dioxide	Cab-O-Sil	Godfrey L. Cabot
Hexamethylenediamine carbamate	HMDA	E.I. du Pont de Nemours and Company, Inc.
Triethylenetetramine	TETA	Fisher Scientific Company
Benzothiazole disulfide	MBTS	E.I. du Pont de Nemours and Company, Inc.
2-Mercaptoimidazoline	Na22	E.I. du Pont de Nemours and Company, Inc.
Hydrated silica	HiSil 233	Columbia-Southern Chem Corp.
Silica	HiSil 303	Columbia-Southern Chem Corp.
Tetramethylthiuram disulfide	TMDS	E.I. du Pont de Nemours and Company, Inc.
Phenol-formaldehyde resin	Durex 12687	Hooker Chemical Corporation
40% Dicumyl peroxide	DiCup 40	Hercules Powder Company
Dibasic lead phosphate	DyPhos	National Lead Corporation
Silicon-treated HiSil 233	Silstone 110	Stoner Rubber Company
50% Dichlorobenzoyl peroxide	Cadox TS-50	Cadet Chemical Corporation
High-abrasion furnace black	Philblack "O"	Phillips Petroleum Company

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13. ABSTRACT  Terpolymers were synthesized to give nitroso rubbers having improved processing characteristics and improved low-temperature properties. The terpolymers fall into six types: aromatic-containing, bromine- or chlorine-containing, hydrogen-containing, diene-containing, ester-containing, and miscellaneous. Processing studies were conducted based on the reactive chemical sites contained in the terpolymer. Low-temperature property studies were confined to differential thermal analysis determinations of the second-order transition, T <sub>g</sub> , temperatures. The best processing results were obtained with dichlorobenzoyl peroxide crosslinked esters. The low-temperature properties of the terpolymers show promise for an improved processible nitroso rubber.		

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymerization	8					
Compounding	8					
Testing	8					
Nitroso rubber	2					
Terpolymers	2					
Copolymers	1					
Bromine	1					
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Curing	4					

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